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(54) Title: PROCESS FOR THE PREPARATION OF TRIHYDROCARBYLSILYLATED CARBOXYLATE MONOMERS

(57) Abstract: The present invention provides a process for the preparation of trihydrocarbylsilylated unsaturated carboxylate monomers comprising the step of reacting, in the presence of a catalyst, an hexahydrocarbyldisiloxane with an unsaturated carboxylic anhydride.

Process for the preparation of trihydrocarbylsilylated carboxylate monomers.

Field of the invention

The invention relates to a new method for the preparation of trihydrocarbylsilylated carboxylate monomers

Background of the invention

Antifouling paints are used to prevent and delay the fouling of underwater structures (e.g. ships' bottom, docks, fishnets, and buoys) by various marine organisms such as shells, seaweed, and aquatic bacteria. When such marine organisms adhere and propagate on an underwater structure like the bottom of a ship, the surface roughness of the whole ship may be increased to the point of inducing a decrease of velocity of the ship or an increase of fuel consumption. Further, removal of such aquatic organisms from the ship's bottom needs much labour and a long period of working time in a costly dry dock. In addition, if these organisms adhere and propagate on an underwater structure such as a steel structure, they deteriorate the anticorrosive coating films leading to a reducing of the lifetime of the underwater structure.

Underwater structures are therefore coated with antifouling paint employing polymers containing various hydrolysable groups and more specifically organosilyl groups.

Amongst those antifouling paints is for example, an antifouling paint of the hydrolysable self-polishing type proposed in WO 84/02915 and JP 63215780 A, which employs a (meth)acrylic ester polymer having triorganosilyl groups in the side chains. Other examples of patents and patent applications related to the use of organosilyl acrylate polymers in antifouling compositions are EP

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131626, US 4593055, US 4594365, JP 63118381 A, EP 0775733, WO 96/38508, EP 802243, EP 0714957, JP 07018216 A, JP 01132668 A, JP 05077712 A, JP 01146969 A and US 4957989, which are hereby incorporated by reference.

Some of the polymers used in the above-described antifouling paints are based on silylated carboxylate monomers.

Several processes are known for the synthesis of silylated carboxylate monomers.

JP 5306290 A discloses a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid with a halogenoalkylsilane (e.g. trialkylsilylchloride) in the presence of a tertiary amine compound having a cyclic structure. This process has disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields as a by-product a hydrogen halide (which provokes the corrosion of the production equipment) or a halide salt (which has to be removed by filtration).

A synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described by A.Chapman & A.D.Jenkins in J.Polym.Sci. Polym.Chem.Edn. vol 15, p.3075 (1977).

JP 10195084 A discloses the reaction of unsaturated carboxylic acids such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst. One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic anhydride due to a side reaction of the produced H_2 on the carbon-carbon double bond.

J.Valade describes in "Compte Rendu de l'Académie des Sciences" n° 246, p. 952-953 (1958) the reaction of hexamethyldisiloxane or hexaethyldisiloxane

with acetic anhydride or benzoic anhydride in the presence of zinc chloride whereas maleic anhydride or succinic anhydride do not react with hexamethyldisiloxane or hexaethyldisiloxane in the presence of zinc chloride.

Therefore, an object of the present invention is to provide a novel process capable of readily preparing trihydrocarbylsilylated unsaturated carboxylate monomers in a high yield.

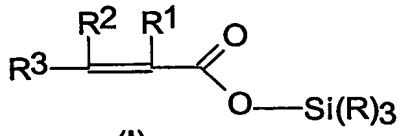
Another object of the present invention is to provide a novel process preparing said monomers from easily available starting materials.

A further object of the present invention is to provide a novel process offering an improvement vis-à-vis of the disadvantages disclosed above.

The present invention is based on the reaction of either linear or cyclic unsaturated carboxylic anhydrides with hexahydrocarbyldisiloxane to synthesise, in the presence of a catalyst, trihydrocarbylsilylated unsaturated carboxylate monomers.

Summary of the invention

The present invention relates to a new process for the preparation of trihydrocarbylsilylated unsaturated carboxylate monomers of either general formula (I)



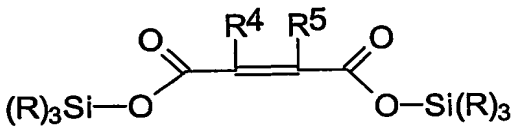
(I)

wherein

each R independently represents an alkyl, a substituted alkyl, an aryl or a substituted aryl group, R^1, R^2 each independently represents a hydrogen atom or an alkyl or substituted alkyl group, an aryl or a substituted aryl group, R^3

represents a hydrogen atom, an alkyl or substituted alkyl group, an aryl or a substituted aryl group or $-COOR^6$ wherein R^6 represents an alkyl, a substituted alkyl, an aryl or a substituted aryl group,

or general formula (II)



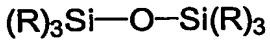
(II)

wherein

each R is as already defined above

R^4, R^5 each independently represents a hydrogen atom or an alkyl or substituted alkyl group, an aryl or substituted aryl group

which process comprises the step of reacting, in the presence of a catalyst, a hexahydrocarbyldisiloxane of formula (III)

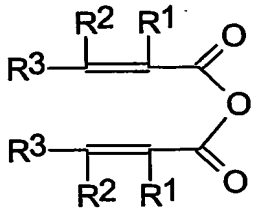


(III)

wherein

R is as already defined above

either with an unsaturated carboxylic anhydride of formula (IV),

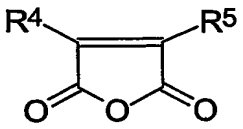


(IV)

wherein

R^1, R^2, R^3 are as already defined above

or with an unsaturated carboxylic anhydride of formula (V)



(V)

wherein R^4, R^5 are as already defined above.

Preferably, the catalyst used in the present invention consists of a mixture of a strong acid and a nucleophilic base.

(For the purposes of clarity general formula (II) has been depicted separately but may also be considered as an alternative of formula (I) wherein R^6 represents $-Si(R)_3$ with R as already defined above).

The term "alkyl", as used herein unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10

carbon atoms, more preferably 1 to 8 carbon atoms, still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Said radical may be a substituted alkyl group, i.e. optionally substituted with one or more substituents independently selected from alkyl, aryl, alkoxy, halogen, hydroxy or amino radicals. Examples of such alkyl radicals may be independently selected from methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, iso-amyl, n-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl and the like.

In a preferred embodiment R, R^1, R^2, R^3, R^4, R^5 and R^6 each independently represent a linear, branched, or cyclic or polycyclic alkyl, substituted alkyl, aryl or substituted aryl group, saturated or unsaturated, containing from 1 to 12 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms, yet more preferably R is 4 carbon atoms. Preferably, R is chosen from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, sec-butyl, t-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, n-amyl, iso-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl, phenyl or substituted phenyl, and the like. More preferably, R is chosen from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, sec-butyl, t-butyl, 2,3-dimethylbutyl, n-amyl, n-hexyl, n-octyl, t-octyl, n-dodecyl, lauryl, phenyl or substituted phenyl wherein the substituents may be linear or branched alkyl, aryl, halogene, alkoxy, phenoxy or nitro. Yet in a more preferred embodiment R is n-butyl, or isopropyl.

In a preferred embodiment R^1, R^2, R^3, R^4 and R^5 each independently represent hydrogen atom or a methyl group.

The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be a substituted aryl group ie optionally substituted with one or more substituents independently

selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-methylphenyl, stearyl, phenethyl, (2-methyl)-phenethyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and the like.

As used herein, the term "independently" indicates that each radical R so described, can be identical or different.

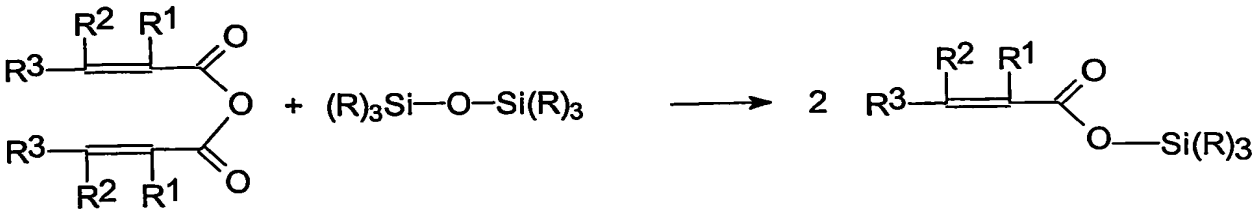
In the embodiment when R^3 is $-COOR^6$, the trihydrocarbylsilylated unsaturated carboxylates of general formula (I) and the unsaturated carboxylic compound (IV) can be of either cis (maleic) or trans (fumaric) configuration.

In a more preferred embodiment the trihydrocarbylsilylated unsaturated carboxylates obtained by the process of the invention are trihydrocarbylsilyl acrylates or trihydrocarbylsilyl methacrylates.

The present invention will be further disclosed in detail hereunder.

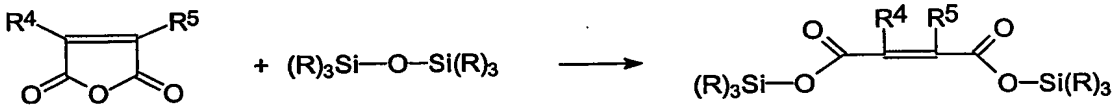
Detailed description of the invention

The present invention relates to a new process for the synthesis of trihydrocarbylsilylated unsaturated carboxylates according either to the general scheme 1:



(IV) (III) (I)

or to the general scheme 2 :



(V) (III) (II)

Unsaturated carboxylic anhydride represented by the above formula (**IV**) or (**V**) is mixed with hexahydrocarbyldisiloxane of formula (**III**) with or without solvent. Examples of solvents, which can be used in the process according to the invention, include hexane, cyclohexane, toluene, xylene, pentane, heptane, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthalene, diethylether, diisopropyl ether, diisobutyl ether, THF, Dioxane, dichloromethane or mixtures thereof. Preferably, an inert solvent is used, more preferably, a hydrocarbon inert solvent such as hexane, cyclohexane, toluene or xylene.

The reaction may be conducted with an added polymerisation inhibitor. Preferably, a radical polymerisation inhibitor is used. A suitable polymerisation inhibitor is o-methoxyphenol. The reaction progress may be monitored by any suitable analytical method.

Preferably, the solvent is at least 10 wt% of the total reaction mix at the start of the reaction, more preferably, at least 20 wt%, most preferably, at least 30 wt%. The reaction may also be without solvent and accordingly suitable

ranges of solvent are 0-99 wt% of the total reaction mix, more preferably, 20-80 wt%, most preferably 30-70 wt%.

Examples of unsaturated carboxylic anhydrides, which can be used in the process according to the invention include acrylic anhydride, methacrylic anhydride, crotonic anhydride, angelic anhydride, tiglic anhydride, maleic anhydride, citraconic anhydride (methylmaleic anhydride).

Examples of the trihydrocarbylsilylated unsaturated carboxylate monomers prepared by the process of the invention using (meth)acrylic anhydride include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, tri t-butylsilyl (meth)acrylate.

Other examples include ethyldimethylsilyl methacrylate, n-butyldimethylsilyl methacrylate, bis(trimethylsilyl) itaconate, t-butyl dimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyldi-n-butylsilyl (meth)acrylate, diisopropylstearylsilyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyldiphenylsilyl (meth)acrylate, phenyldimethylsilyl (meth)acrylate, n-hexyldimethylsilyl (meth)acrylate, tert-octyldimethylsilyl (meth)acrylate, phenethyldimethylsilyl (meth)acrylate, (2-methyl)-phenethyldimethylsilyl (meth)acrylate, (2,3-dimethylbutyl)dimethylsilyl (meth)acrylate, cyclohexyldimethylsilyl (meth)acrylate and lauryldiphenylsilyl (meth)acrylate.

Examples of the trihydrocarbylsilylated unsaturated carboxylate monomers prepared by the process of the invention using maleic anhydride include bis triisopropylsilyl maleate, bis tri-n-butylsilyl maleate, bis t-butyldiphenylsilyl

maleate, bis t-butyldiphenylsilyl maleate or the corresponding fumarate isomers.

The reaction is conducted in the presence of a catalyst comprising of, more preferably consisting of, a mixture of a strong acid and a nucleophilic base. By "strong acid", we mean an acid having a pKa value preferably less than 5, more preferably less than 2, and most preferably less than -5. Preferably, the "strong acid" is stronger than acetic acid, more preferably stronger than chloroacetic acid, most preferably, stronger than trichloroacetic acid. By "nucleophilic base", we mean a base having an available electron pair for donation. More specifically, by 'nucleophilic base', we mean an organic Lewis base having an electron pair available for interacting in a reversible manner with the acylation agent, more preferably the base is a nitrogen containing molecule which is more basic than triethylamine, more preferably this amine is a heteroaromatic amine, more preferably an heteroaromatic mono or polyamine substituted or not with one or more amino groups, more preferably an heteroaromatic mono or polyamine substituted or not with one or more amino groups in which at least one of the nitrogen electron pairs is conjugated with the aromatic ring in such a manner that it brings an increase in negative charge on another amino function of the molecule.

Among strong acids that can be used, one can cite sulfuric acid, phosphoric acid, chlorhydric acid, bromhydric acid, hydriodic acid, nitric acid, trifluoromethanesulfonic acid or perfluoroalkylsulfonic acids, methanesulfonic acid, para-toluene sulfonic acid, trifluoroacetic acid. A preferred strong acid is trifluoromethanesulphonic acid. Strong ion exchange resins (sulfonated styrene copolymers) such as Amberlyst® 15 resin (CAS RN = 39389-20-3) or perfluoroalkylsulfonic resins such as Nafion® NR50 resin (CAS RN = 118473-68-0) may also be used. Among nucleophilic bases that can be used, one can cite pyridine, 2- (dimethylamino)pyridine, 4-(dimethylamino)pyridine, 4-piperidino pyridine, 4-(4-methylpiperidino)pyridine, 4-pyrrolidinopyridine, 4-morpholinopyridine, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, polymer- bound dimethylaminopyridine (examples of which

may be found in US 4997944 incorporated herein by reference), 1-methylbenzimidazole, 2-methylbenzimidazole, benzimidazole and, in addition, N-methyl imidazole(NMI), N,N-dimethylamino pyridine(DMAP), hexamethylphosphoric triamide(HMPA), 4,4 dimethyl imidazole, N-methyl–2-pyridone(NMP), pyridine N-oxide, triphenylphosphine oxide, tributyl phosphine, 2,4 dimethyl pyridine, N-methyl-4-pyridone, ZnCl2, 3,5 dimethyl pyridine, imidazole, trimethylamine, triethylamine, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, and montmorillonites such as K10 or KSF.

Preferred nucleophilic bases include 2- (dimethylamino)pyridine, 4-(dimethylamino)pyridine, 4-(4-methylpiperidino)pyridine, 4-pyrrolidinopyridine, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, polymer-bound dimethylaminopyridine, 1-methylbenzimidazole, 2-methylbenzimidazole, benzimidazole. A more preferred nucleophilic base is 4-(dimethylamino) pyridine or derivatives thereof.

Preferably, the catalyst is present at a level of 0.2-40 mol % (mol/mol siloxane), more preferably 1-24 mol %, most preferably 2-10 mol % in the reaction medium at the start of the reaction. In a batch process, the catalyst level relative to moles of siloxane in the starting reaction medium will increase during the reaction, whereas in a continuous process the catalyst level will remain relatively constant throughout the process except towards the end of any such process when it may rise relative to the level of siloxane as feed reactants are no longer added to the process.

Preferably the molar ratio of strong acid to nucleophilic base in the catalyst is in the range 1:10 to 10:1, more preferably, 1:5 to 5:1, most preferably 1:2 to 2:1. Especially preferred is a range between 3:2 to 2:3, more especially preferred is a ratio of approximately 1:1.

The reaction is preferably carried out at a temperature between 30°C and 130°C, more preferably between 40°C and 120°C, and most preferably between 50°C and 100°C, for example at 60°C or 90°C.

Preferably, the reaction takes place in less than 24 hours, more preferably, less than 20 hours, more preferably less than 12 hours.

Preferably, the polymerisation inhibitor is present in the range 0.001-10% wt/wt of the total reaction mix, more preferably 0.001-5% wt/wt and most preferably 0.01-2% wt/wt.

Preferably, the molar ratio of siloxane:anhydride is between 1:100 and 50:1, more preferably between 10:1 and 1:10, most preferably, between 2:1 and 1:2. Preferably, the molar ratio of siloxane:anhydride is approximately 1:1.

The reaction may be carried out at any convenient pressure, for instance atmospheric pressure.

The advantage of this invention is that the process uses reactants, which can be easily handled. Hexahydrocarbyl disiloxanes may be considered as easily accessible since they are formed as a by-product during acidic deprotection of silyl protected reactive functional groups such as e.g. alcohols, amines or carboxylic acids (as described in "Protective Groups in Organic Synthesis" T.W.Greene and P.G.M.Wuts J.Wiley & Sons, 1999).

Another advantage lies in the simplicity and safety of the procedure (no by-products, hence no trapping of corrosive gaseous matter).

Due to its one step process, the present invention is a substantial improvement over the existing methods.

Moreover, due to the possibility of using numerous hexahydrocarbyldisiloxanes as reactants leading to the production of a wide range of trihydrocarbylsilylated unsaturated carboxylate monomers, the process of the present invention is a substantial improvement over the existing methods.

The trihydrocarbylsilylated unsaturated carboxylate monomers obtained by the process of the invention can be polymerised with various other monomers such as vinyl monomers including acrylic esters, methacrylic esters, styrene, vinyl esters (e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl benzoate), vinyltoluene, alpha-methylstyrene, crotonic esters, and itaconic esters.

The polymers and copolymers of said monomers are useful in coating or paint composition. More preferably they are used in antifouling coating or paint compositions.

The antifouling coating compositions prepared using the monomers obtained by the process of the invention are tin-free coatings and provide an alternative to the present self-polishing coating technology based on hydrolysable tributyltin polymers (the use of which is due to be banned in antifouling paints by 2003). The trihydrocarbylsilylated unsaturated carboxylate monomers provided by the process of the invention compared to organotin monomers are less toxic, less polar, more hydrophobic and more stable.

The invention will now be described by way of illustration only and with reference to the accompanying examples.

Examples and comparatives examples

All the monomers used in the examples and comparative examples are purchased from Aldrich and used without any preliminary purification.

In examples 1 and 2, NMR datas have been determined in $CDCl_3$ and are expressed as delta versus TMS.

Example 1 (according to the invention)

285 mg of 4-(dimethylamino)pyridine and 352 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 3.8g of hexamethyldisiloxane and 3.6g of methacrylic anhydride. The solution heated at 60°C for 16h to furnish trimethylsilyl methacrylate.

Trimethysilyl methacrylate: ^{13}C NMR : 167.7, 137.6, 127.1, 18.2, -0.257 ; ^{29} Si NMR : 24.3; IR (film): 2963, 1703, 1335, 1256, 1178, 874, 854 cm^{-1}.

Example 2 (according to the invention)

146 mg of 4-(dimethylamino)pyridine and 180 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 5g of hexabutyldisiloxane and 1.8g of methacrylic anhydride. The solution was heated at 60°C for 16h to furnish tributylsilyl methacrylate.

Tri-n-butylsilyl methacrylate: ^{13}C NMR : 167.8, 137.9, 126.0, 26.7, 25.5, 18.5, 13.5, 14.0; ^{29} Si NMR : 23.1; IR (film): 2959, 2927, 1703, 1334, 1174, 886, 766 cm^{-1}.

Example 3 (according to the invention)

185 mg of 4-(dimethylamino)pyridine and 228 mg of trifluoromethanesulfonic acid were successively added, at room temperature, to a mixture of 5 g of hexaisopropyldidiloxane and 2.33 g of methacrylic anhydride. The solution was heated at 90°C for 24 h to furnish triisopropylsilyl methacrylate

Triisopropylsilyl methacrylate: ^{13}C NMR: 167.7, 138.0, 126.2, 18.8, 18.1, 2.4; ^{29}Si NMR: 21.8; IR (film): 2949, 2870, 1703, 1334, 1178, 884, 751 cm^{-1}.

Comparative example 1 (according to J.Valade in Compte Rendu de l'Académie des Sciences n° 246, p. 952-953 (1958))

8.4 g of zinc chloride were added, at room temperature, to a mixture of 5 g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 110°C. After 16h no transformation was observed.

Comparative example 2: (catalyst is strong acid only)
352 mg of trifluoromethanesulfonic acid were added, at room temperature, to a mixture of 5 g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

Comparative example 3: (catalyst is nucleophilic base only)
285 mg of 4-(dimethylamino)pyridine were added, at room temperature to a mixture of 5g of hexamethyldisiloxane and 6.25 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

Comparative example 4: (catalyst is strong acid and weak nucleophilic base)
185 mg of pyridine and 352 mg of trifluoromethanesulfonic acid was added, at room temperature, to a mixture of 3.8 g of hexamethyldisiloxane and 3.6 g of methacrylic anhydride. The solution was heated at 60°C. After 16h no transformation was observed.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

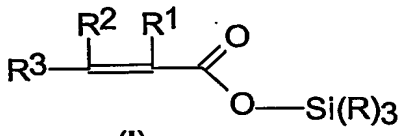
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims

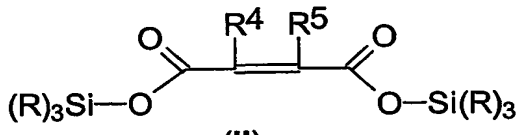
1. Process for the preparation of trihydrocarbylsilylated unsaturated carboxylate monomers of either general formula (I)



(I)

wherein
each R independently represents an alkyl, a substituted alkyl, an aryl or a substituted aryl group,
R^1, R^2 each independently represents a hydrogen atom or an alkyl or substituted alkyl group, an aryl or substituted aryl group
R^3 represents a hydrogen atom, an alkyl or substituted alkyl group, an aryl or substituted aryl group, or $-COOR^6$ wherein R^6 represents an alkyl, a substituted alkyl, an aryl group or a substituted aryl group,

or general formula (II)



(II)

wherein
each R is as already defined above

R^4, R^5 each independently represents a hydrogen atom or an alkyl or substituted alkyl group, an aryl or substituted aryl group

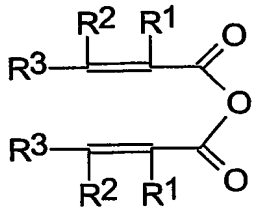
which process comprises the step of reacting, in the presence of a catalyst, a hexahydrocarbyldisiloxane of formula (III)

$$(R)_3Si—O—Si(R)_3$$

(III)

wherein
R is as already defined above

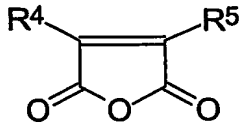
either with an unsaturated carboxylic anhydride of formula (IV),



(IV)

wherein
R^1, R^2, R^3 are as already defined above

or with an unsaturated carboxylic anhydride of formula (V)



(V)

wherein R^4, R^5 are as already defined above.

2. A process according to claim 1, wherein R and R^6 each independently represent a linear, branched, or cyclic or polycyclic alkyl, substituted alkyl, aryl or substituted aryl group, saturated or unsaturated, containing from 1 to 12 carbon atoms.

3. A process according to claim 1, wherein R and R^6 each independently represent a linear, branched, or cyclic or polycyclic alkyl, substituted alkyl, aryl or substituted aryl group, saturated or unsaturated, containing from 1 to 6 carbon atoms.

4. A process according to claim 1, wherein R and R^6 each independently represent a linear, branched, or cyclic or polycyclic alkyl, substituted alkyl, aryl or substituted aryl group, saturated or unsaturated, containing from 1 to 4 carbon atoms.

5. A process according to claim 1, wherein R is chosen from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, sec-butyl, t-butyl, 2-methylbutyl, 2,3-dimethylbutyl, lauryl, pentyl, n-amyl, iso-amyl, n-hexyl, cyclohexyl, 3-methylpentyl, n-octyl, t-octyl, n-dodecyl, phenyl or substituted phenyl, and the like.

6. A process according to claim 2 wherein R each independently are chosen from the group of methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, t-butyl, phenyl or substituted phenyl.

7. A process according to claim 6 wherein R are n-butyl or isopropyl.

8. A process according to claim 6 wherein phenyl is substituted by linear or branched alkyl, aryl, halogene, alkoxy, phenoxy or nitro.

9. A process according to any of the preceeding claims, wherein the unsaturated carboxylic anhydrides of formula (IV) are selected from the group consisting of acrylic anhydride, methacrylic anhydride, crotonic anhydride, angelic anhydride, and tiglic anhydride.

10. A process according to any of the preceeding claims, wherein the unsaturated carboxylic anhydrides of formula (V) are selected from the group consisting of maleic anhydride, and citraconic anhydride.

11. A process according to any of the preceeding claims, wherein the catalyst comprises a mixture of a strong acid and a nucleophilic base.

12. A process according to claim 11, wherein the catalyst consists of a mixture of a strong acid and a nucleophilic base.

13. A process according to any preceding claim, wherein the strong acid has a pka value less than 5.

14. A process according to any preceding claim, wherein the nucleophilic base is a base having an available electron pair for donation.

15. A process according to any preceding claims, wherein the acids are independently selected from sulfuric acid, phosphoric acid, chlorhydric acid, bromhydric acid, hydriodic acid, nitric acid, trifluoromethanesulfonic acid or perfluoroalkylsulfonic acids, methanesulfonic acid, para-toluene sulfonic acid or trifluoroacetic acid.

16. A process according to any preceding claim, wherein the nucleophilic bases are independently selected from pyridine, 2-

(dimethylamino)pyridine, 4-(dimethylamino)pyridine, 4-piperidino pyridine, 4-(4-methylpiperidino)pyridine, 4-pyrrolidinopyridine, 4-morpholinpyridine, imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, polymer- bound dimethylaminopyridine (examples of which may be found in US4997944 incorporated herein by reference), 1-methylbenzimidazole, 2-methylbenzimidazole, benzimidazole and, in addition, N-methyl imidazole(NMI), N,N-dimethylamino pyridine(DMAP), hexamethylphosphoric triamide(HMPA), 4,4 dimethyl imidazole, N-methyl–2-pyridone(NMP), pyridine N-oxide, triphenylphosphine oxide, 2,4 dimethyl pyridine, N-methyl-4-pyridone, $ZnCl_2$, 3,5 dimethyl pyridine, imidazole, trimethylamine, triethylamine, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole and montmorillonites such as K10 or KSF.

17. A process according to claim 11, 12, 14 or 16 wherein the strong acid is a strong ion exchange resin.

18. A process according to any preceding claim, wherein the molar ratio of strong acid to nucleophilic base in the catalyst is in the range 1:10 to 10:1.

19. A trihydrocarbylsilylated unsaturated carboxylate monomer as defined in formula I produced by a process in accordance with any one of claims 1-18.

INTERNATIONAL SEARCH REPORT

Interna Application No
PCT/E /01990

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, WPI Data, EPO-Internal, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 13, 30 November 1998 (1998-11-30) & JP 10 212293 A (NITTO KASEI CO LTD;NOF CORP), 11 August 1998 (1998-08-11) abstract	1-18
X	& DATABASE MACHINE TRANSLATION JPO 'Online! Japanese Patent Office; "http://www4.jpdl.jpo.go.jp/cgi-bin/tran_web_cgi_eije" Database accession no. JP 10 212293 paragraph '0036! - paragraph '0039!; examples 1-3	19

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INTERNATIONAL SEARCH REPORT

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 May 2003	17/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richter, H

INTERNATIONAL SEARCH REPORT

Interna Application No
PCT/E[redacted]3/01990

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 403 169 A (HERGENROTHER PAUL M ET AL) 24 September 1968 (1968-09-24) example VIII	1-18
A	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. Reaction ID 673962 XP002205020 abstract	1-18
A	& VALADE: COMPTE RENDU DE L'ACADEMIE DES SCIENCES, no. 246, - 1958 pages 952-953, cited in the application	1-18
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 2322813 XP002240418 abstract & MIRONOV ET AL.: CHEM. HETEROCYCL. COMPD. (ENGL. TRANSL.), no. 5, 1969, pages 167-171,	19
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 2351835 XP002240423 abstract & ANDREEVA ET AL.: J. GEN. CHEM. USSR, no. 30, 1960, pages 2763-2765,	19
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 2412288 XP002240424 abstract & PUKHNAREVICH ET AL.: RUSS. J. GEN. CHEM, vol. 66, no. 8, 1996, pages 1257-1259,	19

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 2409969 XP002240425 abstract & COUFFIGNAL R. ET AL.: TETRAHEDRON LETT, 1978, pages 3713-3716, ---	19
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 4369442; BRN 4368137 XP002240426 abstract & BELLASSOUED M. ET AL.: SYNTHESIS, no. 9, 1983, pages 745-746, ---	19
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 2254838 XP002240427 abstract & FEDOTOV ET AL.: J. GEN. CHEM. USSR, no. 39, 1969, pages 779-784, ---	19
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. BRN 1368535 XP002240428 abstract & BRADY ET AL.: J. ORG. CHEM., vol. 44, 1979, pages 733-737, -----	19

INTERNATIONAL SEARCH REPORT

International application No.
/EP 03/01990

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty of claim 19. So many documents were retrieved that it is impossible to determine which parts of claim 19 may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim is impossible. Consequently, the search has been restricted to the compounds according to claim 19 where R1 and R2 are H; R is unsubstituted alkyl and R3 is H, unsubstituted alkyl or unsubstituted aryl.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Intern: Application No
PCT/E /01990

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10212293 A	11-08-1998	NONE	
US 3403169 A	24-09-1968	NONE	